Cauchy violation and charge transfer potentials

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1. Introduction

Chemical potential equalization (CPE) models [1–3] provide a promising way of constructing force fields with environment-dependent parameters, which can be used to study a system's behavior at the microscopic level. In polarizable force fields, the atomic charges serve as a linkage between the electronic distribution in the system and its instantaneous structure at the atomic level. We adress the question of how a violation of the Cauchy relation and its slope for small temperatures and ambient pressures is reproduced by several CPE models while applying them to ionic compounds. Charge equilibration (QE) models considered in this study are the electronegativity equalization model (EEM) and the split-charge equilibration (SQE) model.

2. Interatomic potential

Force field form used: $V_{\text{tot}} = V_{\text{QE}} + V_{\text{SR}}$

The explicit form of the energy within charge equilibration model is

$$V_{\text{QE}}(\mathbf{Q},\mathbf{q}) = \underbrace{\sum_i \left[\chi_i Q_i + \frac{1}{2}\kappa_i Q_i^2\right]}_{\text{atomic electronegativity and hardness}} + \underbrace{\sum_i \sum_{j>i} \frac{\kappa_{ij}^s}{2} q_{ij}^2}_{\text{bond hardness}} + \underbrace{\frac{1}{2}\sum_i \sum_{j\neq i} J(r_{ij}) Q_i Q_j}_{\text{Coulomb interaction}}$$

Atomic charges $Q_i = \sum_j q_{ij}$ are the sum of all shared partial charges.

Assuming a Gaussian-type distribution of electron density, the **long-range interaction** potential $J(r_{ij})$ has the form

$$J(r_{ij}) = \frac{\text{erf}(\alpha_{ij} r_{ij})}{r_{ij}}$$

the **short-range interaction** potential V_{SR} is taken to be central and pairwise

$$V_{\text{SR}} = \sum_{ij} A_{ij} e^{-r_{ij}/\rho_{ij}}$$

The parameters of the short-range potential were chosen to reproduce the experimental lattice constant of NaCl.

- Atomic radii $\to 0 \Rightarrow$ point charge approximation
- true charges minimize the energy V_{QE}.

3. Cauchy violation and QE

Cauchy relation and violation

In a crystal where particles interact through central pair forces, the elastic tensor $C_{\alpha\beta\gamma\xi}$ possesses complete symmetry in its four indices, thus providing relations between components. These equalities are known as the Cauchy relations. For a crystal of cubic symmetry only one equation remains

$$C_{12} = C_{44}$$

In real crystals the Cauchy relation no longer holds, and the violation $C_{44} - C_{12}$ should be considered instead. This deviation can arise from vibrational contributions to the elastic constants, or from many-body interactions. If the temperature factor is negligible, then one should expect the violation is due to three-body and higher order forces.

Wallace [4] pointed out that experiments on wave propagation in materials under hydrostatic pressure show a combination of elastic coefficients, which is either the combination of wave propagation coefficients or Birch elastic constants.

In the present work we use the Voigt elastic constants. which are defined as the second derivative of the free energy F with respect to the Eulerian strain tensor components $\{\epsilon_i\}_{i=1}^6$

$$C_{ij} = \frac{1}{V}\frac{\partial^2 F}{\partial\epsilon_i \partial\epsilon_j}$$

Charge equilibration in NaCl

True charges for an ideal rocksalt structure are $Q = \frac{-\tilde{\chi}}{\tilde{\kappa} - \alpha_{\text{M}}/a}$,

where $\tilde{\chi} = (\chi_{\text{Na}} - \chi_{\text{Cl}})/2$ - effective electronegativity

and $\tilde{\kappa} = (\kappa_{\text{Na}} + \kappa_{\text{Cl}} + \kappa^s_{\text{NaCl}}/6)/2$ - effective hardness

a is the distance between two nearest Na and Cl atoms.

Electrostatic energy is then $V_{\text{QE}} = \frac{-\tilde{\chi}^2}{2(\tilde{\kappa} - \alpha_{\text{M}}/a)}$,

where α_{M} is a generalized Madelung constant, which includes the effects of screening.

When a structure is deformed the charges will re-adjust to minimize the energy. This leads to the Cauchy violation

$$C_{44} - C_{12} = \frac{1}{V}\frac{Q^2}{\tilde{\kappa} - \alpha_{\text{M}}/a}\left(\frac{\partial\alpha_{\text{M}}}{a\partial\epsilon_1}\right)^2$$

Effect of screening on the Cauchy violation

If we increase screening in the system, then

- the electrostatic interaction $J(r_{ij})$ reduces $\Rightarrow$ Madelung constant α_{M} and its slope are reduced
- the atomic charge Q is reduced
- the electrostatic interaction is reduced
- the lattice constant is reduced (if we assume that the short-range potential V_{SR} remains the same)

$\Longrightarrow$ Screening effects reduce Cauchy violation

First pressure derivative of the Cauchy violation for NaCl

$$\left.\frac{\partial(C_{44}-C_{12})}{\partial P}\right|_{P=0} = \frac{C_{44}-C_{12}}{B_0}\left[\frac{5}{3} + \frac{\alpha_{\text{M}}/a}{\tilde{\kappa} - \alpha_{\text{M}}/a} - V\frac{\partial}{\partial V}\left(\frac{\partial\alpha_{\text{M}}}{\partial\epsilon_1}\right)^2\left(\frac{\partial\alpha_{\text{M}}}{\partial\epsilon_1}\right)^{-2}\right]$$

where B_0 is bulk modulus at zero pressure.

Typical assumption is that screening coefficient α_{ij}, which depends on the ionic radii, does not depend on the interatomic distance. In this case, each term in the sum to construct the Madelung constant depends on volume, which makes the Madelung constant volume-dependent.

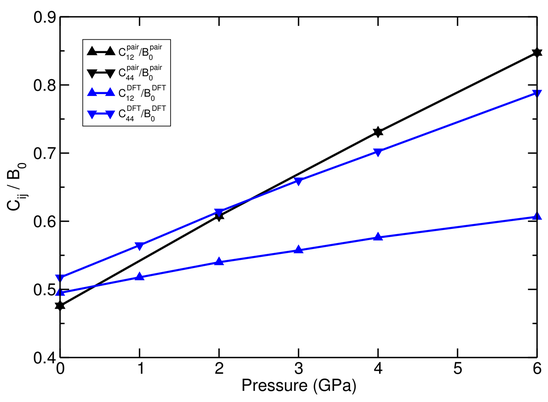
The most simple but still representative assumption is the assumption of **point charges**:

$$C_{44} - C_{12} = \frac{1}{V_p}\cdot\frac{Q^2}{\tilde{\kappa} - \alpha_M/a}\left(\frac{\alpha_{\text{M}}}{3a}\right)^2 > 0 \quad \textbf{strictly positive}$$

$$\left.\frac{\partial(C_{44} - C_{12})}{\partial P}\right|_{P=0} = \frac{C_{44}-C_{12}}{B_0}\left[\frac{5}{3} + \frac{\alpha_{\text{M}}/a}{\tilde{\kappa} - \alpha_{\text{M}}/a}\right] > 0 \quad \textbf{strictly positive}$$

The point charge approximation predicts strictly positive signs for both the Cauchy violation and its first pressure derivative taken at equilibrium at small temperatures.

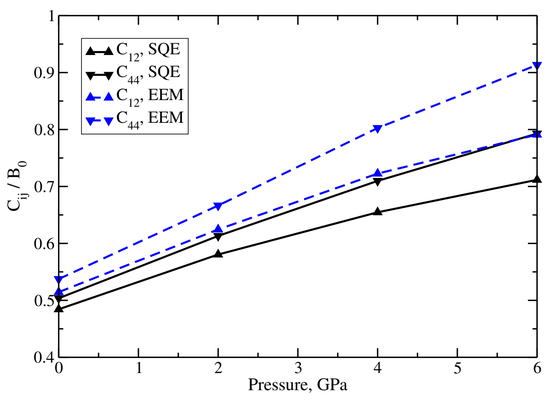
4. Results: Cauchy violation in NaCl



Dependence of normalized elastic constants C_{12}/B_0 and C_{44}/B_0 on pressure obtained from DFT (blue) and from pairwise interaction function (black).

For a two-body potential the two lines coinside. Consequently, Cauchy relation holds for a fixed charge model.

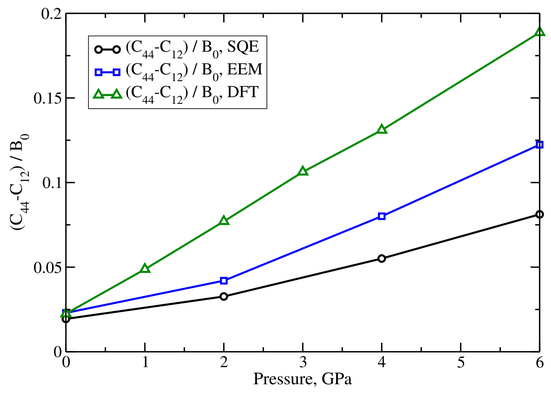
The pairwise potential was fit to DFT data to produce cohesive energy, lattice constant, bulk modulus and elastic constant C_{11} with sufficient accuracy. Nevertheless, it overestimates the slope of elastic constants C_{12} and C_{44} in comparison to DFT results.



Dependence of normalized elastic constants C_{12}/B_0 and C_{44}/B_0 on pressure obtained with EEM (blue) and with SQE model (black).

EEM and SQE model provide similar behaviour of elastic constants C_{12} and C_{44}.

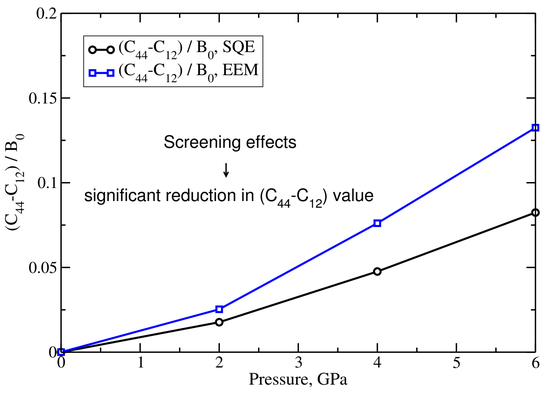
Force field that uses SQE model as a long-range interaction potential is "softer" than the one which uses EEM: SQE models is "harder" in terms of the amount of charge transferred, which implies that the electrostatic energy is reduced. Consequently, the lattice spacing increases, and the crystal becomes softer.



Dependence of normalized Cauchy violation $(C_{44} - C_{12})/B_0$ on pressure obtained from DFT (green), by EEM (blue) and SQE model (black). Models assumed point charges.

Effect of screening on Cauchy violation can be described by the following considerations. If we increase screening, then

- the charge within QE concept decreases and, consequently, long-range attraction decreases. If we assume that the short-range interaction remains the same, then the lattice constant must increase. This factor decreases Cauchy violation.
- the electrostatic interaction potential $J(r) = \text{erf}(\alpha r)/r$ decreases and becomes smoother, which reduces significantly Madelung constant and its derivative. This factor greatly decreases Cauchy violation.



Dependence of normalized Cauchy violation $(C_{44} - C_{12})/B_0$ on pressure given by EEM (blue) and SQE model (black) in the case of introduced screening.

Method	$C_{44} - C_{12}$	$\partial(C_{44} - C_{12})/\partial P$
DFT (PBE-PAW)	0.54 GPa	$0.59 > 0$
DFT [5]	1.41 GPa	$0.18 > 0$
EEM (no screening)	0.49 GPa	$1.51 > 0$
SQE (no screening)	0.20 GPa	$1.02 > 0$
Two-body	0.00 GPa	$0.00 > 0$
experiment [6]	1.49 GPa(*)	$0.21(*) > 0$

(*) the values are given for a finite temperature of $T = 180$K. By reducing the temperature Cauchy violation and its derivative increase, thus making it possible to provide conclusions for lower temperatures.

5. Conclusions

- Both considered QE models reproduce the correct sign of Cauchy violation for rocksalt
- screening affects the value of Cauchy violation crucially: the deviation is reduced significantly
- pressure derivative sign of Cauchy violation in the proximity of ambient pressures for low temperatures is correctly predicted by a spherically symmetric QE model with constant κ^s
- negative Cauchy violation for rocksalt structure may be achieved by including higher order terms in energy expansion: dipole-dipole and charge-dipole terms

References

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